Effect of Thermal Annealing on Optical Properties of Carbon Nitride Nanostructures Synthesized by Discharge-Induced Reaction of Methane and Ammonia

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Abstract
In this work, effect of thermal annealing on the optical characteristics of carbon nitride nanostructures synthesized by discharge-induced reaction of methane and ammonia was studied. These nanostructures were annealed at 200°C, 300°C, and 400°C and then their absorbance and energy band gaps were compared to those of as-prepared nanostructures. It was found that the annealing leads to decrease the absorbance and enlarge energy band gap from 2.6 to 2.77 eV for the sample annealed at 400°C.

Keywords: carbon nitride; Nanostructures; Optical characteristics; Methane-ammonia reaction
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1. Introduction

Carbon nitride has many formulas resulted from the bonding of carbon and nitrogen atoms, however, dicyanodiazomethane with the formula of C_3N_4 or $(CN)_2.C.N_2$ is one of the most important ones and has a 3D structure [1,2]. It has two solid covalent network compounds: beta (β-C_3N_4) and graphitic (g-C_3N_4). The first is predicted to be harder than diamond while the second has very important catalytic properties [3].

Carbon nitride nanostructures are synthesized and prepared by various methods and techniques such as photoreduction [4], thermal evaporation [5], polymerization of some organic compounds [6], laser ablation in liquids [7], chemical vapor deposition [8], plasma decomposition of methane and molecular nitrogen [9], ball-milling at high temperatures [10], plasma-enhanced chemical vapor deposition [11], laser pyrolysis [12], RF reactive magnetron sputtering [13], ion beam assisted sputtering [14] and shock-wave compression of organic C-N-H precursors [15].

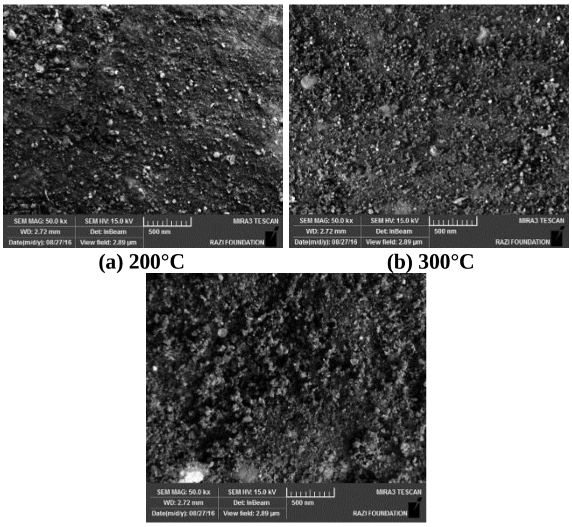
In this work, the dependencies of absorbance and energy band gap of carbon nitride nanostructures synthesized by discharge-induced reaction of methane and ammonia were determined as functions of thermal annealing temperatures.

2. Experimental Part

Deposition camber is first evacuated down to 10^{-5} mbar to remove any residuals or contaminants. Argon gas at pressure of 0.5 mbar was used to generate the fast glow discharge between two electrodes made of stainless steel. The discharge power from a power supply (5-6kV, 4-5A) is applied between the electrodes as pulses of different durations (0.1, 0.25 and 1ms). A pulse forming network (PFN) was used to convert the DC signal of the power supply into short pulses. The repetition rate of discharge pulses could be determined from 1 to 100 Hz by the PFN circuit. However, all results presented here were obtained using repetition rate of 20 Hz. The methane (CH_4) and ammonia (NH_3) gases are premixed in a cooled reactor before pumped into the chamber at flow rate of 1 sccm. This reactor is cooled down to 5°C to prevent the normal reaction of methane and ammonia. The maximum pressure of gas mixture is 3 mbar. As soon as the breakdown of argon gas occurs, the remaining power induces the reaction between CH_4 and NH_3 molecules to form C_3N_4 molecules. This reaction occurs faster than the normal reaction. The synthesized nanoparticles were collected on a clean watch glass (2cm in diameter) inside the chamber. The chamber was kept closed during the application of discharge power throughout valves on the inlets of gases and outlet to the vacuum pump.

3. Results and Discussion

Figure (2) shows the FE-SEM image of the C_3N_4 nanostructures prepared in this work. The particles are mostly separated from each other as no severe aggregation is seen. The average particle size is ranging within 15-30 nm, which may means that the annealing process has no reasonable effect on the structural characteristics and particle size, which may not necessarily be associated with the optical characteristics as the latter depend mainly on the distribution of nanostructures and hence the volumetric density of these nanostructures.



(a) 200°C (b) 300°C

(c) 400°C

Fig. (2) FE-SEM image of C_3N_4 nanostructures annealed at different temperatures

The effect of the thermal annealing process on the structural and morphological characteristics of the C_3N_4 nanostructures can be much more observable at annealing temperatures higher than 400°C because the thermal properties of this material are comparable to those ceramic materials due to the high specific heat of carbon and nitrogen forming this material [16].

Figure (3) shows the effect of thermal annealing on the absorption spectra of the C_3N_4 nanostructures prepared in this work. It is clear that the sample annealed at higher temperature exhibit lower absorbance because the higher temperature induce the carbon and nitrogen atoms not contributing to the formation of C_3N_4 molecules but still exist in the final sample to bond or support the formed molecules [17]. Therefore, the density of C_3N_4 molecules is increased and hence the absorption of C and N atoms – especially in the UV region – is decreased. In the visible region, the absorbance still low for all samples. Consequently, the energy band gap of the prepared samples was determined and found to increase with increasing annealing temperature for the same reason mentioned before. Energy band gap was determined to be 2.675, 2.73, and 2.77 eV for the samples annealed at 200°C, 300°C, and 400°C, respectively, compared to 2.6 eV for the as-prepared sample.

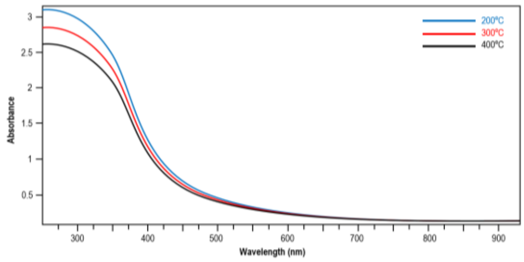


Fig. (3) Absorption spectra of C_3N_4 nanostructures annealed at different temperatures

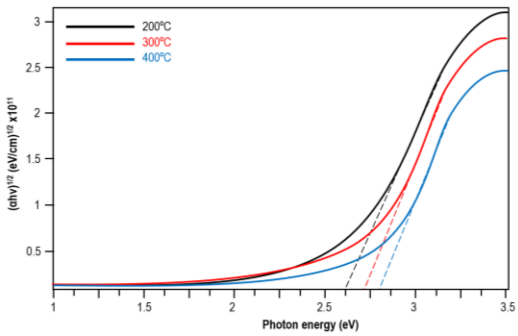


Fig. (4) Variation of absorption coefficient of C_3N_4 nanostructures annealed at different temperatures with photon energy

4. Conclusions

In this work, effect of thermal annealing on the optical characteristics of C_3N_4 nanostructures synthesized by discharge-induced reaction of methane and ammonia was studied. These nanostructures were annealed at 200°C, 300°C, and 400°C and then their absorbance and energy band gaps were compared to those of as-prepared nanostructures. It was found that the annealing leads to decrease the absorbance and enlarge energy band gap from 2.6 to 2.77 eV for the sample annealed at 400°C.

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